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The Effect of High Heating Rate on the Pyrolysis of Carbon/Phenolic Composites

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The pyrolysis of a carbon/phenolic sample has been investigated as a function of
heating rate (from 0.167 K/sec to 30000 K/sec) and has been modeled by assuming two
mechanisms are operating: a process with a low energy of activation which dominates at
low heating rates and a process with a high energy of activation which becomes
important at high heating rates. Kinetic and modeling parameters for the sample
pyrolysis at each heating rate are reported and have been used to accurately
reconstruct the sample thermographs. In addition, the high heating rate instrument/
method is described in detail.

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THE EFFECT OF HIGH HEATING RATE ON THE PYROLYSIS
OF CARBON/PHENOLIC COMPOSITES

INTRODUCTION

The effect of heating rate on the pyrolysis of polymeric and composite materials has been extensively studied using thermal gravimetric analysis (TGA) techniques[1-7]. The maximum heating rates used in these studies have usually been less than several thousand degrees per minute (~ 20 K/sec) and material behavior under these conditions has been well documented.[1,2,5] Material behavior under conditions of high heating rate (>10000 K/sec) has recently become of great interest because of the need to predict high performance material behavior in harsh thermal environments and to accurately model the interaction of directed energy with polymeric and composite materials, especially with respect to material blowoff resulting from the generation of internal gas pressures. The behavior of materials under conditions of high heating rates has usually been inferred by extrapolating the low rate data - a generally unreliable procedure.[2,7]

In this work, we report on the effect of bulk heating rates (ranging from 0.167 K/min to 30000 K/sec) on the pyrolysis of a carbon/phenolic composite material. The high heating rates have been achieved using a resistance heating system which we have recently designed and constructed at the Naval Research Laboratory (NRL). Kinetic parameters describing the pyrolysis have been obtained using a modified Friedman approach.[8]

EXPERIMENT

HIGH HEATING RATE INSTRUMENT

Figure 1 shows a cross-sectional and 3-D schematic view of the high rate resistive heating instrument: an adaptation from coal gasification studies and earlier polymer pyrolysis studies.[9-13] The sample is placed between two stainless steel screen filaments (250 mesh) the ends of which are clamped together and joined to the conductor blocks (See Fig. 1). A quartz or pyrex retaining tube is placed over the filaments and sealed with Viton o-rings to the inside ends of the brass conductor blocks. One outside block end is terminated with a gas chromatograph (GC) septum so that samples of the pyrolysis vapors can be obtained. The other outside end is connected to a vacuum line for sample chamber evacuation or purging with a controlled atmosphere. With this instrument design, it is possible to examine sample pyrolysis under conditions of varying partial vacuums and atmosphere composition.

Heating is achieved by passing a large current through the stainless steel screen filaments. A pulse shaping network controls the heating rate and peak temperature. Figure 2a shows a block diagram of the electronic control network and Figure 2b shows details of the pulse shaping unit. To vary the heating rate, the length of the resistive wire immersed in the water tank, Fig. 2a, is varied. This causes both the rate and the final temperature to change. Heating rates of 30000 K/sec, with maximum temperatures of 1200°C, have been reproducibly obtained with this setup. At present, the maximum attainable temperature is 1200°C, the melting point of the stainless steel screen. Plans are underway to increase the maximum temperature by using other filament materials.

The temperature is monitored, in real-time, using an optical pyrometer which limits measurements to temperatures greater than 450°C. Attempts at measuring the temperature using a thermocouple (chromel-alumel, 5 mils) spot-welded to the screen were not successful. Tests indicated that the thermocouple became part of the resistive heating circuit, drawing off some of the heating current.

The effect of heating rate on sample pyrolysis is determined by monitoring the production of pyrolysis vapors as a function of time, heating rate and peak temperature. The pyrolysis is normally conducted in a vacuum (~50-100 mtorr) and the production of vapors measured as a function of time using a sensitive pressure transducer (See Table 1). Pressure and temperature data are collected as a function of time on a high speed, multi-channel strip-chart recorder and later digitized for analysis (Fig. 3). Plans are underway to automate the data collection.

TABLE 1. PRESSURE TRANSDUCERS

TRANSDUCER MODEL	PRESSURE RANGE	OUTPUT RANGE
Edwards Type 600 Barocell Sensor	0 - 10 torr	0 - 10 V dc
MKS Baratron Pressure Meter Type 144	0 - 10 torr	0 - 1 V dc
OMEGA Model PX176	0 - 15 PSIA	0 - 5 V dc
OMEGA Model PX304	0 - 50 PSIA	0 - 0.1 V dc

EXPERIMENT PROCEDURE

SAMPLE PREPARATION

Composite samples are prepared as a fine powder (200 micron diameter or less). Polymeric samples have not been examined, but could be prepared as a fine powder or a thin film (thickness less than 200 micron). The 200 micron limit to the sample size is based on theoretical work which indicates that for particles of this size or smaller, gas diffusion out of the particle is not the rate limiting step at heating rates on the order of 10000 K/sec.[12,14] In addition, carbon/phenolic composite particles of this size are calculated to reach thermal equilibrium quickly:[12,14] Assuming a 200 micron sphere of carbon/phenolic

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is simultaneously heated on four sides to 1000°C, the particle center should reach 950°C (95% of the maximum temperature) in less than 20 msec, assuming a constant thermal conductivity, heat capacity and density.[15] Based on this calculation and an examination of our temperature profiles, we believe the actual sample temperatures to be within 10% of the measured values.

Composite pyrolysis samples are prepared as a powder by low-speed drilling completely through the composite panel in several different areas. The drill bit and the composite are left to cool for several minutes between drill-throughs so that the sample does not experience thermal damage. This procedure insures that a true representation of the composite composition is obtained. The powdered material left as the drilling residue is collected and sieved to obtain a powder fraction with a diameter less than 200 microns. Microscopic examinations of sample powders have indicated that the fiber and cured resin matrix are homogeneously distributed. Prior to pyrolysis, the 200 micron powder sample is placed in a drying oven (at 70°C) until it attains an equilibrium weight (several days).

The particular carbon/phenolic sample used in this work was obtained from American Automated Engineering, Inc. The material composition prior to curing was reported as

| Resin Solids | 34.0% |
| Volatile Content | 4.1% |

which results in a carbon fiber content of 61.9% by weight. A carbon content of 63% was measured for the cured composite via a sulfuric/nitric acid digestion in our lab.

FILAMENT PREPARATION/SAMPLE LOADING

The heating filaments used in the carbon phenolic study were prepared by cutting the stainless steel screen into 12cm x 4mm strips and exposing the strips to temperatures between 600 and 700°C, in a flowing inert atmosphere, for 10 to 20 minutes. This heat treatment allowed the stainless steel mesh to expand and anneal and also removed any wire coatings. Recent tests of blank screens and heat-treated blank screens suggest that the contribution of any wire coatings to the pyrolysis vapors is insignificant. Therefore, future studies will not heat-treat the filaments. In addition, with the introduction of the second battery to the pulse shaping network, doubling the voltage to 24 V dc, the filament size has been increased to 12cm x 8mm.

After weighing the blank filament, a small amount of sample (1-3 mg) is spread over the interior of the folded filament. This sample-coated-filament is then pressed between flat plates, for approximately 2 minutes, under a hydrolic load of 12000 - 15000 psi using a Carver Laboratory Press. The pressed sample-coated-filament is weighed and assembled into the pyrolysis instrument.

The pyrolysis is conducted and the filament with any resulting char residue is weighed. Char is considered to be the solid inert material remaining on the screen after the pyrolysis is complete.

It is also necessary to weigh the quartz retaining tube before and after pyrolysis because of the deposition of a thin film onto the tube from condensing pyrolysis vapors. The pyrolysis apparatus is currently being modified to optically monitor the film deposition as a function of time.

DATA MANIPULATION AND HANDLING

The raw data from the chart recorder is digitized using a GRAPHTEC XY PLOTTER (Model MP2300) and a software program developed specifically for the high heating rate pyrolysis experiments. A copy of the source code of this program may be obtained by direct communication with the authors. The digitized data is entered into a LOTUS worksheet developed specifically for determining the kinetic parameters of interest. Copies of the data worksheets are also available on request.

Sample mass (as a function of time) is determined by digitizing the pressure curve within the limits of the starting mass and the mass of the char. This procedure involves the introduction of several assumptions: (1) the rate of deposition of the thin film is identical to the gas formation rate and is included as part of the mass loss; (2) at the time of maximum pressure, all of the sample has been pyrolyzed; and (3) the average temperature of the pyrolysis gases is ~295 K throughout the pyrolysis. Testing the second assumption, a sample was pyrolyzed, the pyrolysis chamber evacuated and the sample repyrolyzed. A negligible pressure increase was observed and interpreted to mean that the sample had been completely pyrolyzed in the previous run. Further support for this assumption was obtained by examining plots of the rate of mass loss as a function of temperature (Fig. 4); the rate of mass loss goes to zero before the sample has cooled to a temperature below the pyrolysis threshold. To test the third assumption, a sample was pyrolyzed and the vapors allowed to come to equilibrium. The sample was then repyrolyzed in the equilibrium gases. Only a small increase in pressure was observed, suggesting that the gas temperature during pyrolysis is not significantly different from room temperature.

The mass fraction remaining as a function of temperature, Fig. 5, is obtained by dividing the remaining sample mass at a particular time by the intial mass (M/Mo) and plotting this value against the sample temperature measured at that time. To determine the rate of mass loss as a function of time, the slope of the line connecting successive mass remaining data points is plotted against the average time of the respective points. Similarly, the rate of mass loss as a function of temperature is obtained using the corresponding average temperature.

PYROLYSIS PRODUCT ANALYSIS

The pyrolysis vapors are analyzed using gas chromatography (GC) and mass spectrometry (MS). Coupling the results of these analysises with the equilibrium vapor pressure after pyrolysis, an effective molecular weight for the pyrolysis products is calculated.

LOW HEATING RATE

Low heating rate (0.167 K/sec) data was obtained for the same carbon/phenolic sample in an N_2 atmosphere using a DuPont Instruments 951 Thermogravimetric Analyzer/1090 Thermal Analyzer System. The pyrolysis data was obtained as a plot of the percent of sample weight remaining versus temperature and was digitized for analysis. The fine powder used in these experiments was not sieved to the 200 micron limit and was also not oven dried.

THEORY AND RESULTS

The pyrolysis of composite and polymeric materials is often represented in terms of a global mechanism. That is, all of the competing and parallel reactions are combined into one, effective overall reaction.

$$SAMPLE \qquad PRODUCTS(VAPOR) \; + \; PRODUCTS(SOLID) \qquad (1)$$
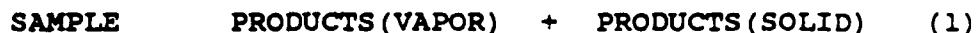
The pyrolysis reaction is described by the kinetic equation given below in Eqn. 2.

$$-d(SAMPLE)/dt = k[SAMPLE]^n \qquad (2)$$

where $-d(SAMPLE)/dt$ is the rate of sample mass loss, [sample] is the concentration of the sample, k is the rate constant and n is the order of the reaction. This global rate equation is the sum of the many individual rate equations involved in the pyrolysis kinetics, as indicated by Eqn. 3.

$$k[SAMPLE]^n = k_1[SAMPLE]^{n_1} + k_2[SAMPLE]^{n_2} + k_3[SAMPLE]^{n_3}$$
$$+ k_4[SAMPLE]^{n_4} + \ldots \ldots \qquad (3)$$

The rates of most reactions increase as the temperature is increased. This temperature dependence is usually expressed by the Arrhenius equation

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$$k = Ae^{-E/RT} \tag{4}$$

where A is known as the pre-exponential factor and is usually regarded as temperature independent, E is the energy of activation, R is the gas constant and T is the absolute temperature.

In elementary reactions, the pre-exponential factor is related to the molecular geometry and/or orientation of reactants while the energy of activation is the energy barrier separating reactants and products. These values are determined by using the logarithmic form of Eqn. 4 and plotting $\ln(k)$ vs $1/T$. If the result is a straight line, the reaction is said to show Arrhenius behavior; E is obtained from the slope ($-E/R$) of the line and A from the intercept ($\ln(A)$).

Substituting the Arrhenius equation (Eqn. 4) for each k in Eqn. 3 results in a temperature dependent expression for the pyrolysis, Eqn. 5.

$$
\begin{aligned}
-d(SAMPLE)/dt &= (Ae^{-E/RT})[SAMPLE]^n \\
&= (A_1 e^{-E_1/RT})[SAMPLE]^{n_1} \\
&\quad + (A_2 e^{E_2/RT})[SAMPLE]^{n_2} \\
&\quad + (A_3 e^{-E_3/RT})[SAMPLE]^{n_3} \\
&\quad + (A_4 e^{-E_4/RT})[SAMPLE]^{n_4} \\
&\quad + \ldots\ldots
\end{aligned}
\tag{5}
$$

The purpose of this work is to determine values for A_i, E_i and n_i which will allow for accurate predictions of mass loss over a wide range of heating rates for the carbon/phenolic sample.

To characterize the effect of heating rate on the pyrolysis of the carbon/phenolic sample, a modified version of the Friedman method is used.[8] The Friedman method is based on the Arrhenius equation and allows kinetic parameters to be determined from data obtained over a wide range of heating rates. Additionally, in this method, the sample concentration term is determined directly from the experiment data.

Friedman's equation is given as[6,7,8]

$$-1/M_O \times dM/dt = Af(M/M_O)e^{-E/RT} \tag{6}$$

where M_O is the original weight of the sample (g), M is the instantaneous weight of the sample (g), dM/dt is the time rate of mass loss (g/sec), $f(M/M_O)$ is an undefined weight function, R is the gas constant, T is the absolute temperature, A is the

Arrhenius pre-exponential factor and E is the Arrhenius energy of activation. Eqn. 6 is used in its logarithmic form

$$\ln(-1/M_O \times dM/dt) = \ln(Af(M/M_O)) - E/RT \qquad (7)$$

where $\ln(-1/M_O \times dM/dt)$ is plotted as a function of $1/T$ for parametric values of M/M_O. The slope of the line tangent to the curve at each point equals $-E/R$ and its intercept, $\ln(Af(M/M_O))$.

We slightly modify the Friedman method and determine energies of activation as a function of heating rate rather than mass fraction remaining (M/M_O) (See Fig. 6). The analysis must be conducted in this fashion because our heating rate range is much greater than that reported by Friedman[8]. That is, the temperature differences between corresponding mass fractions at our different heating rates are significant and therefore, the important pyrolysis reaction(s) may be different at each heating rate for a common mass friction, rendering Friedman's original method inappropriate.

Only the initial energy of activation (defined as the slope up to the point where dM/dt reaches a constant value, Fig. 6) are considered because as the temperature increases, the reactant composition and concentration change and other reaction mechanisms may become important. Therefore, we are only examining the reaction(s) that depend on starting composition.

To obtain the reaction order and pre-exponential factor, the normalized weight function, $f(M/M_O)$, is defined as[2,7]

$$f(M/M_O) = [(M - M_C)/(M_O - M_C)]^n \qquad (8)$$

where M_C, the weight of the char remaining after pyrolysis is complete, is removed from consideration. Multiplying both sides of Eqn. 8 by A and transforming to the logarithmic form gives

$$\ln(Af(M/M_O)) = \ln A + n\ln[(M - M_C)/(M_O - M_C)] \qquad (9)$$

A and n are obtained from the slope and intercept, respectively, of a linear least squares fit to a plot of the recalculated $\ln(Af(M/M_O))$ vs $\ln[(M - M_C)/(M_O - M_C)]$, Fig. 7. (The recalculated $\ln(Af(M/M_O))$ is obtained using the average initial energy of activation for a particular heating rate.) Following Henderson, we separate the plot into two regions and linearly least squares fit each region to determine a regional pre-exponential factor and a reaction order (Table 2).[6,7]

Mass loss thermographs (M/M_O as a function of temperature) were reconstructed for each heating rate using experimentally determined parameters. Accurate reproductions of the thermographs were obtained and are shown with the experiment data in Figs. 8 - 10.

DISCUSSION

The time that the sample dwells in a temperature region is dramatically different for low and high heating rate experiments. Because of this, low energy of activation processes occur to a much lesser extent in high heating rate experiments than in low heating rate experiments. That is, the sample is depleted before the high temperatures are reached in low heating rate experiments, whereas in high heating rate experiments, sample is still present when high temperatures are attained. Therefore, we expect a different set of products for high heating and low heating rate experiments.

The only characterization of the composition of the pyrolysis vapor products for the carbon/phenolic composite is from a calculation of the effective molecular weight of the vapor (Table 2). This calculation is based on the post-pyrolysis equilibrium pressure and gave good reproduciblity for each heating rate. (It was not possible to obtain reproducible, quantitative GC data for the equilibrium pyrolysis vapors for a given heating rate for the carbon/phenolic system due to experimental difficulties.) The observed increase in molecular weight with heating rate can be attributed to a corresponding change in the thermal degradation mechanism, or to further reactions and recombinations of hot pyrolysis gases in cooler regions of the instrument prior to their analysis. Investigations into the possibility of real-time monitoring of specific pyrolysis vapor products are being pursued. Such measurements will be difficult because of the low concentration of products, but if successful, should provide accurate compositions for the pyrolysis vapors. Such information will assist in determining the cause of the molecular weight dependence on heating rate, allowing more detailed kinetic mechanisms of the pyrolysis to be proposed.

The thin, tacky film deposited on the quartz retaining tube during pyrolysis is believed to result from the condensation and/or further reaction of certain of the pyrolysis gases. Analysis of the thin film has proved to be difficult, resisting analysis via gas chromatography. Work is planned to spectroscopically (FTIR and UV/VIS) investigate its composition. In addition, the high heating rate instrument is being modified to optically monitor the rate of deposition of this film in real time.

Fig. 11 shows activation energy (E) as a function of heating rate. The asympotic nature of this curve is derived by assuming two limiting energies of activation over the temperature range examined. We assume the parameters associated with the low heating rate data (0.167 K/min) are an adequate description of the kinetic process with low energy of activation and, similarly, that the process with a high energy of activation is adequately described by the parameters generated from the 30000 K/sec data. It should be possible to fit the data obtained for the heating

rates between these extremes using a weighted sum of the low and high energies of activation processes and such work is currently underway.

Demonstrating the validity of using the reported parameters in modeling material behavior, accurate reproductions of the individual heating rate thermograms over a wide range of heating rates have been generated (Figs. 8 - 10). The reported energies of activation used in the reconstruction can be interpreted as having physical significance; they correspond to collections of reactions and should be viewed as 'mini-global' activation energies. However, the reported A's and n's do not have physical significance; they are parameters which provide the best model of the data over a particular mass fraction range.

The heating rate dependence of the energy of activation for the pyrolysis of the carbon/phenolic sample (Fig. 11) suggests the possibility of such a dependence for char yield (M_C/M_O) and char composition: different activation energies imply different reaction mechanisms, which in turn lead to different products (including char). Our data are somewhat ambiguous in this regard because the heating rate and maximum temperature are not independent. More definitive investigations are required before a general conclusion is made.

CONCLUSION

A high heating rate (~30000 K/sec) pyrolysis instrument has been constructed and successfully used to investigate the effect of heating rate on a carbon/phenolic sample up to 1000°C. Kinetic and modeling parameters have been determined for the processes occurring at temperatures greater than 450°C and are used to produce accurate reconstructions of sample thermographs over a wide range of heating rates.

FUTURE PLANS

Studies of the pyrolysis of several other composite materials, over a wide range of heating rates, are underway and will be reported upon completion. Instrumental modification is being considered in order to monitor film deposition from pyrolysis vapors in real time and to increase the maximum temperature of the experiment.

ACKNOWLEDGEMENT

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TABLE 2. SUMMARY OF RESULTS

HEATING RATE (K/sec)	Estimated Molecular Weight of Vapor	Char Yield (M_C/M_O)	E (kcal/mol) ± 10%	Range of M/M_O	A(sec^{-1})	n
30000	70	0.68	26.2	0.99 - 0.97	1.3E5	1.25
				0.97 - 0.89	1.1E5	0.06
8000	62	0.68	15.4	0.99 - 0.75	1624	0.00
7000	50	0.68	12.0	0.94 - 0.83	602	0.53
				0.83 - 0.75	430	0.12
4000	42	0.77	8.2	0.95 - 0.83	67	0.38
				0.83 - 0.77	43	0.01
0.167	N/A	0.80*	7.5	0.99 - 0.88	1.4	0.94
				0.88 - 0.81	0.9	0.45

* Low heating rate data was limited to a maximum temperature of ~775°C in comparision to the other high heating rate maximum temperatures of ~1000°C.

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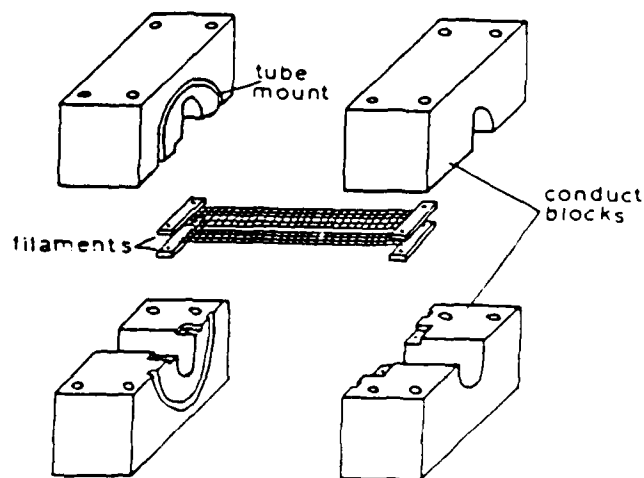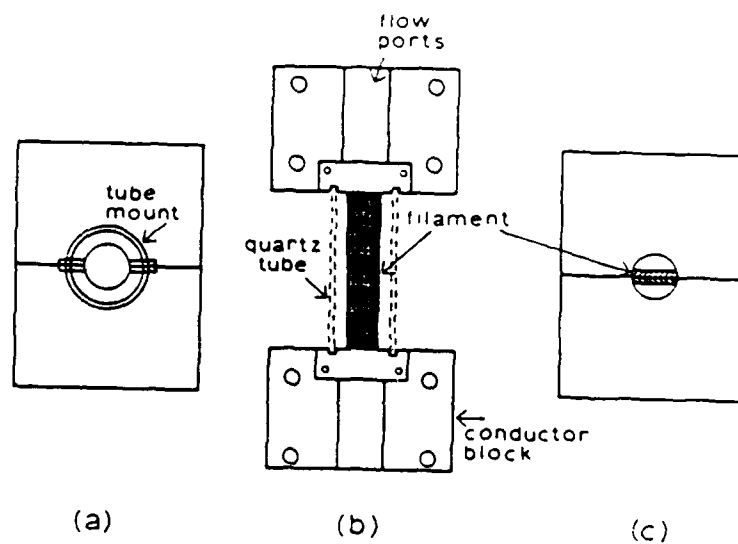
Fig. 1 — Cross-sectional and end-on views of the high rate heated filament instrument (a-c) and a 3-D view showing how the major components are assembled.

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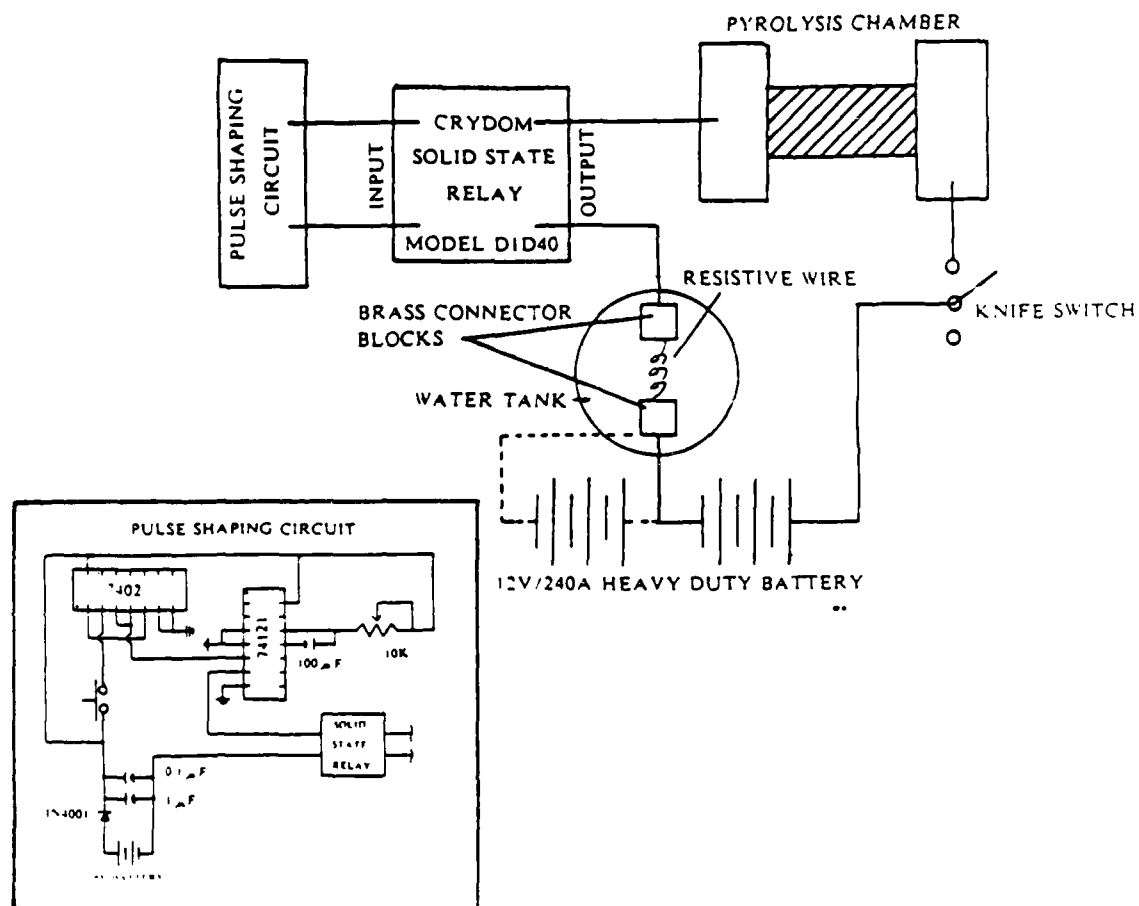
CONTROL NETWORK

Fig. 2 — (a) A block diagram of the electronic control network. To vary the heating rate. the length of the resistive wire in the water tank is varied. For the highest heating rates (> 10000 K/sec) it is necessary to connect the second source battery in series, indicated by the dashed lines. (b) A detailed circuit diagram of the pulse shaping unit.
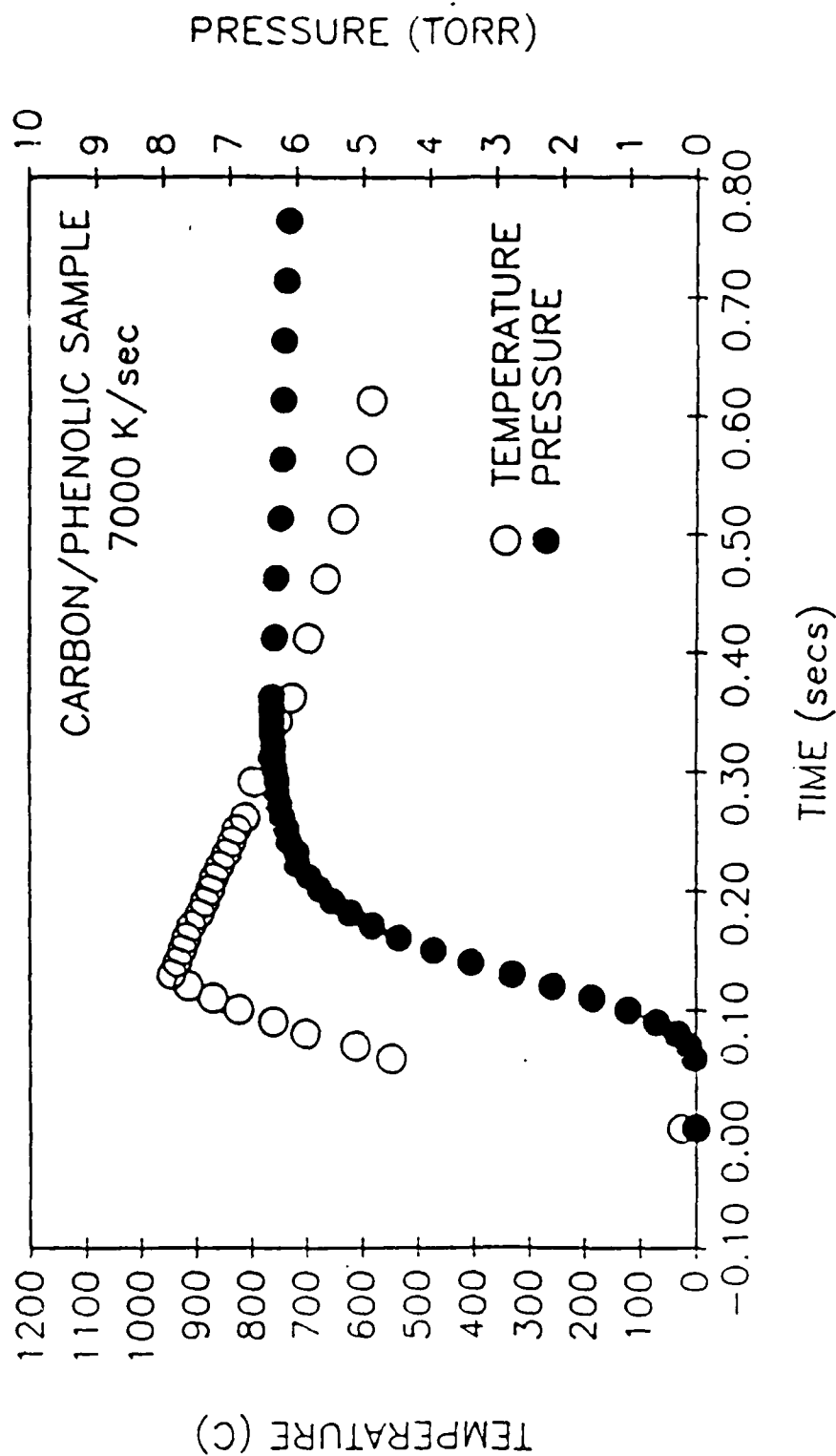
Fig. 3 — Digitized raw temperature and pressure data obtained from the pyrolysis of a carbon/phenolic composite conducted at 7000 K/sec.

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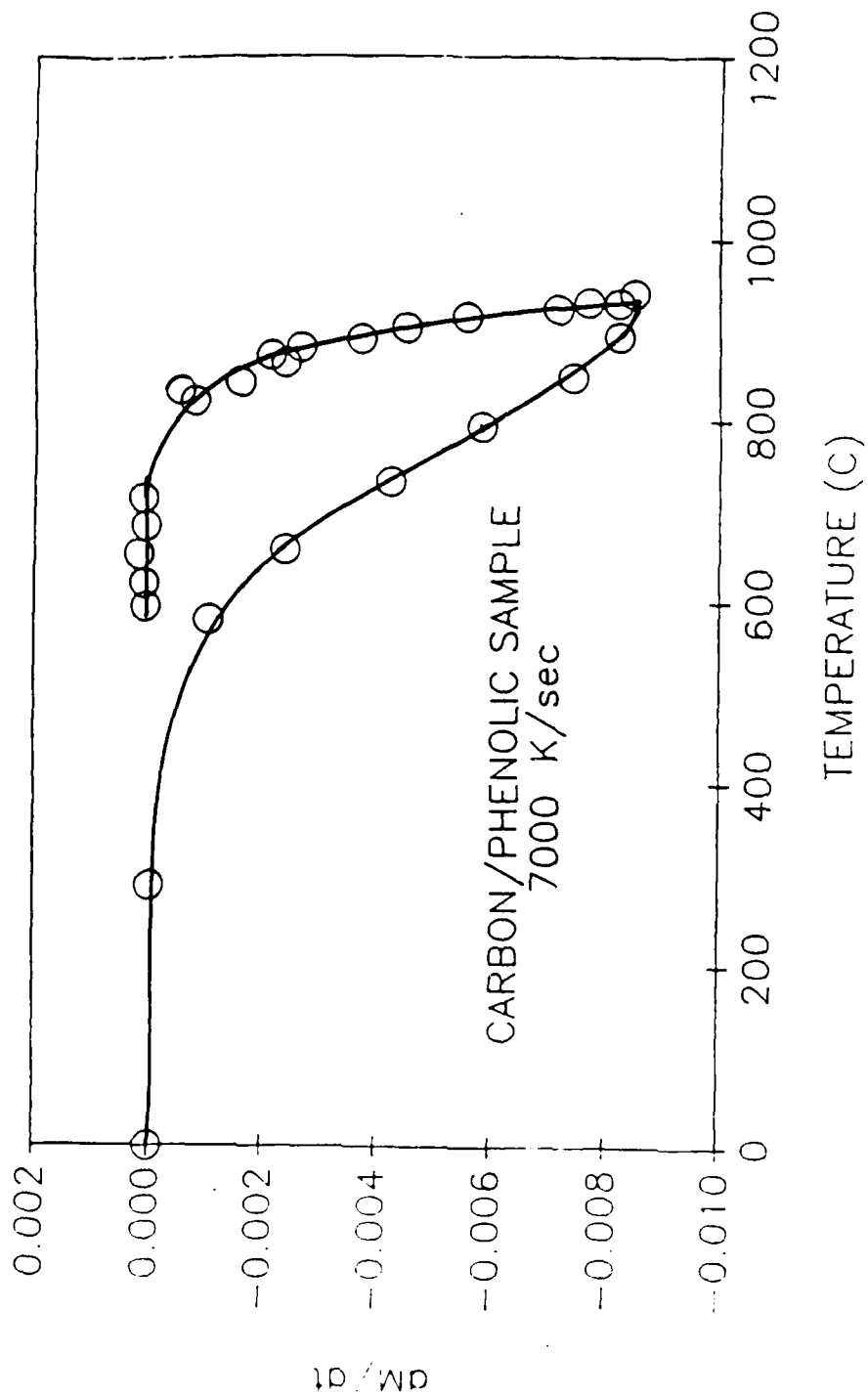
Fig. 4 — Plot of the rate of mass loss as a function of temperature for the pyrolysis of a carbon/phenolic composite at 7000 K/sec. Note that the rate of mass loss goes to zero before the sample temperature drops below the pyrolysis threshold.
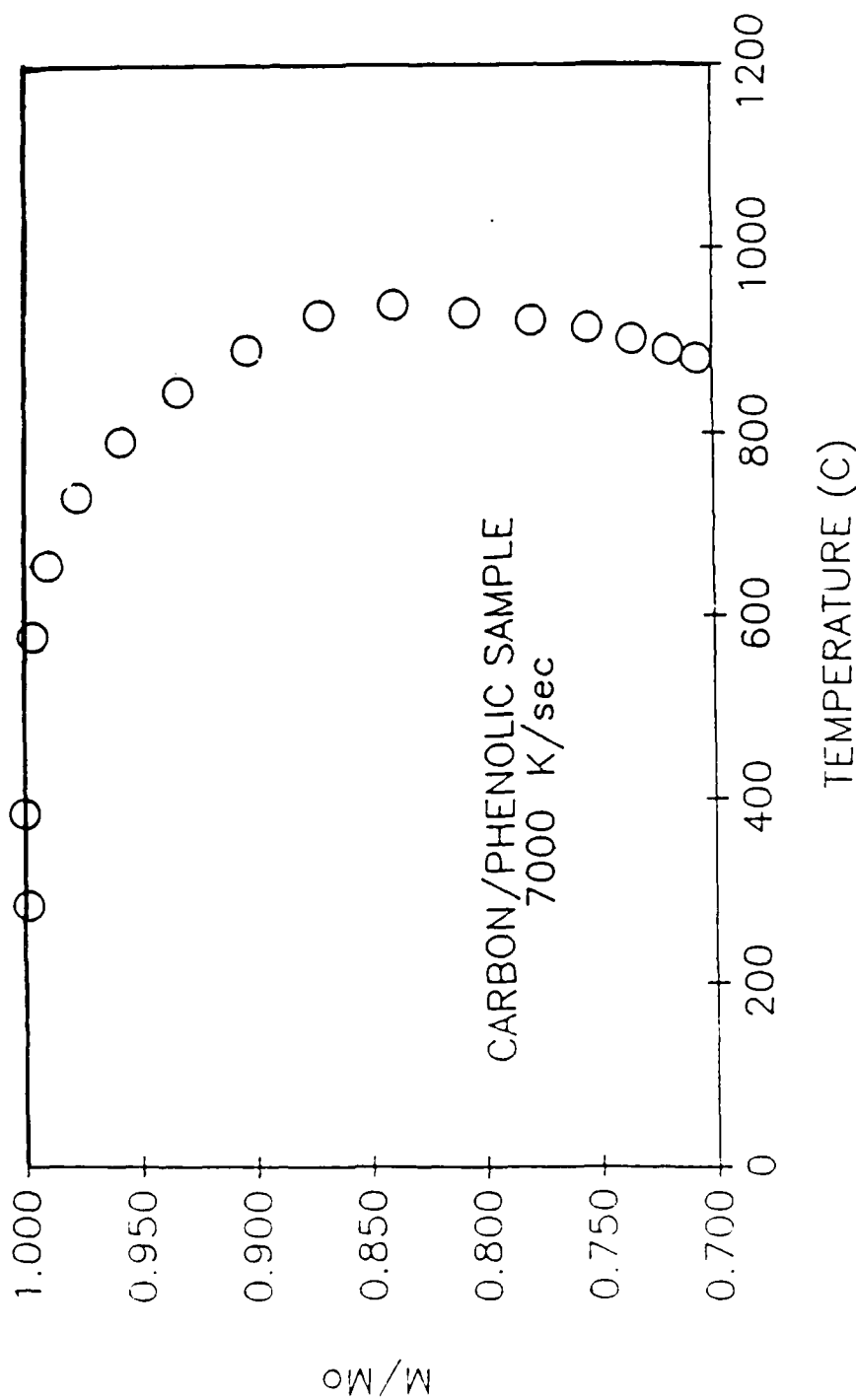
Fig. 5 — Mass fraction remaining (M/M_0) as a function of sample temperature for the pyrolysis of a carbon/phenolic sample at 7000 K/sec.
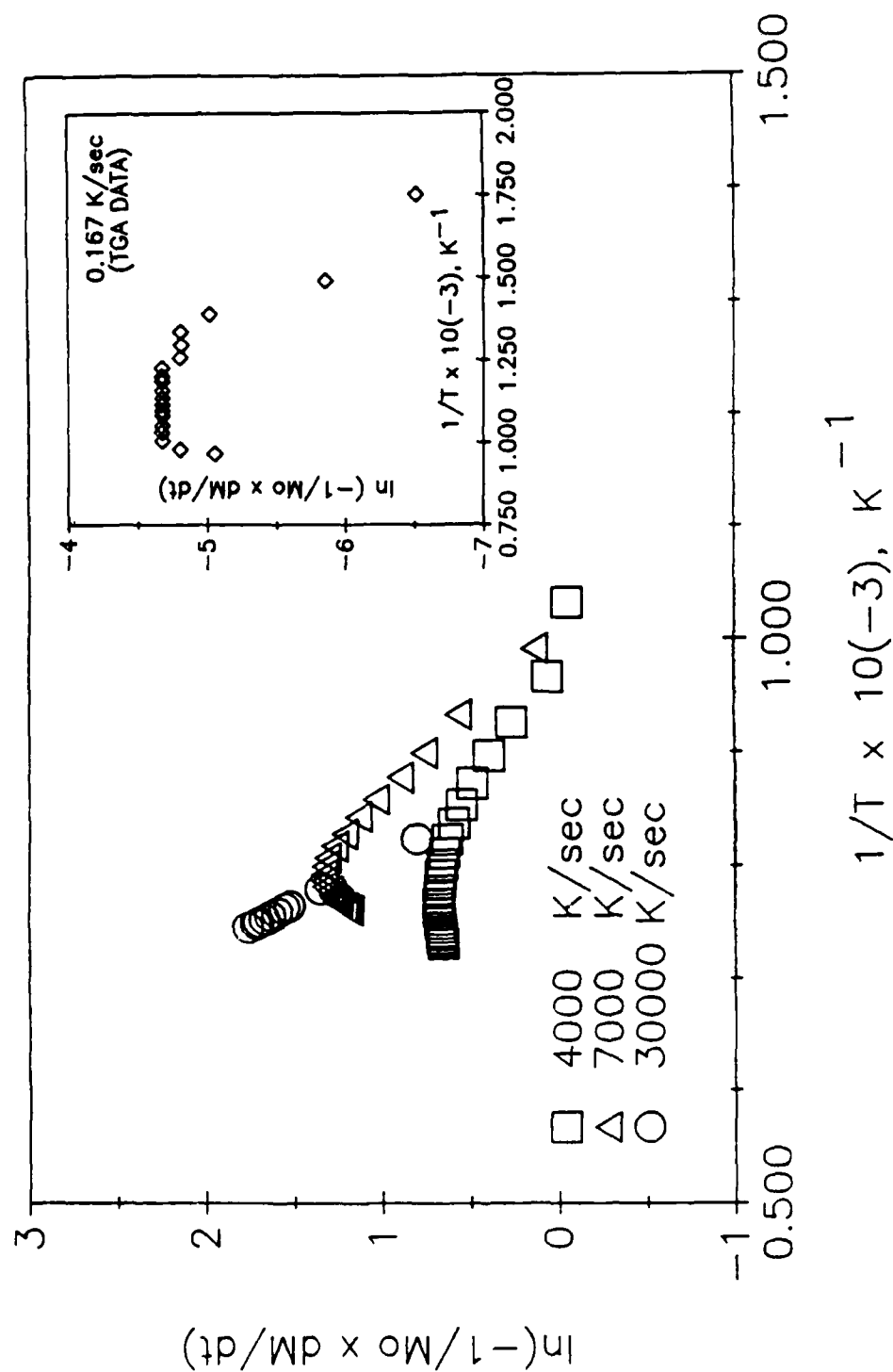
Fig. 6 — Typical plots of the natural logarithm of the derivatives of the rate of mass loss of the carbon/phenolic samples as a function of temperature for four heating rates. Energies of activation were determined from linear least squares fits to the initial data points.
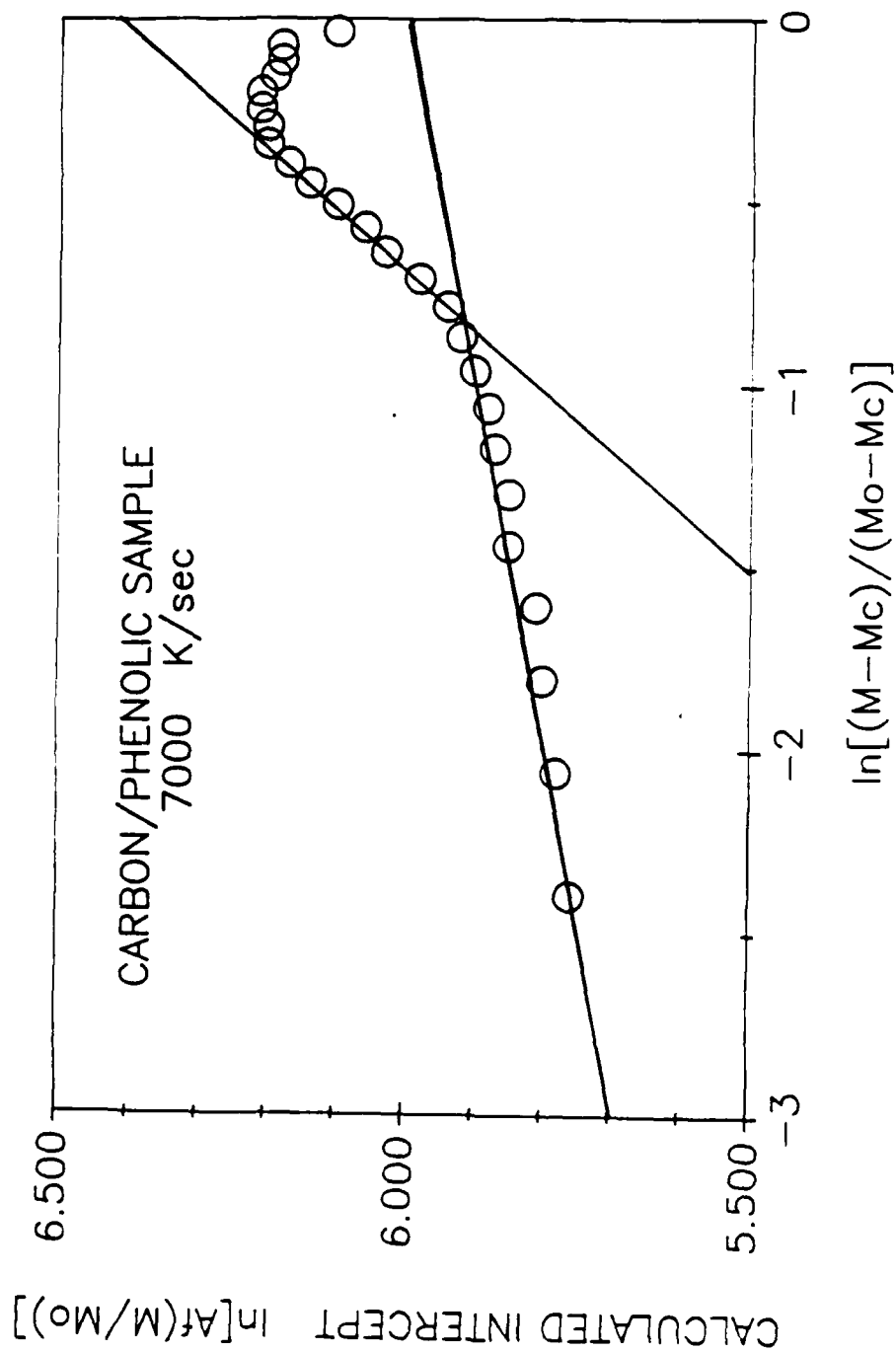
Fig. 7 - The plot to determine n and A for the pyrolysis of a carbon/phenolic sample at 7000 K/sec. The solid lines are least squares fits to the data in each region. The slope of the line gives n and the intercept A.
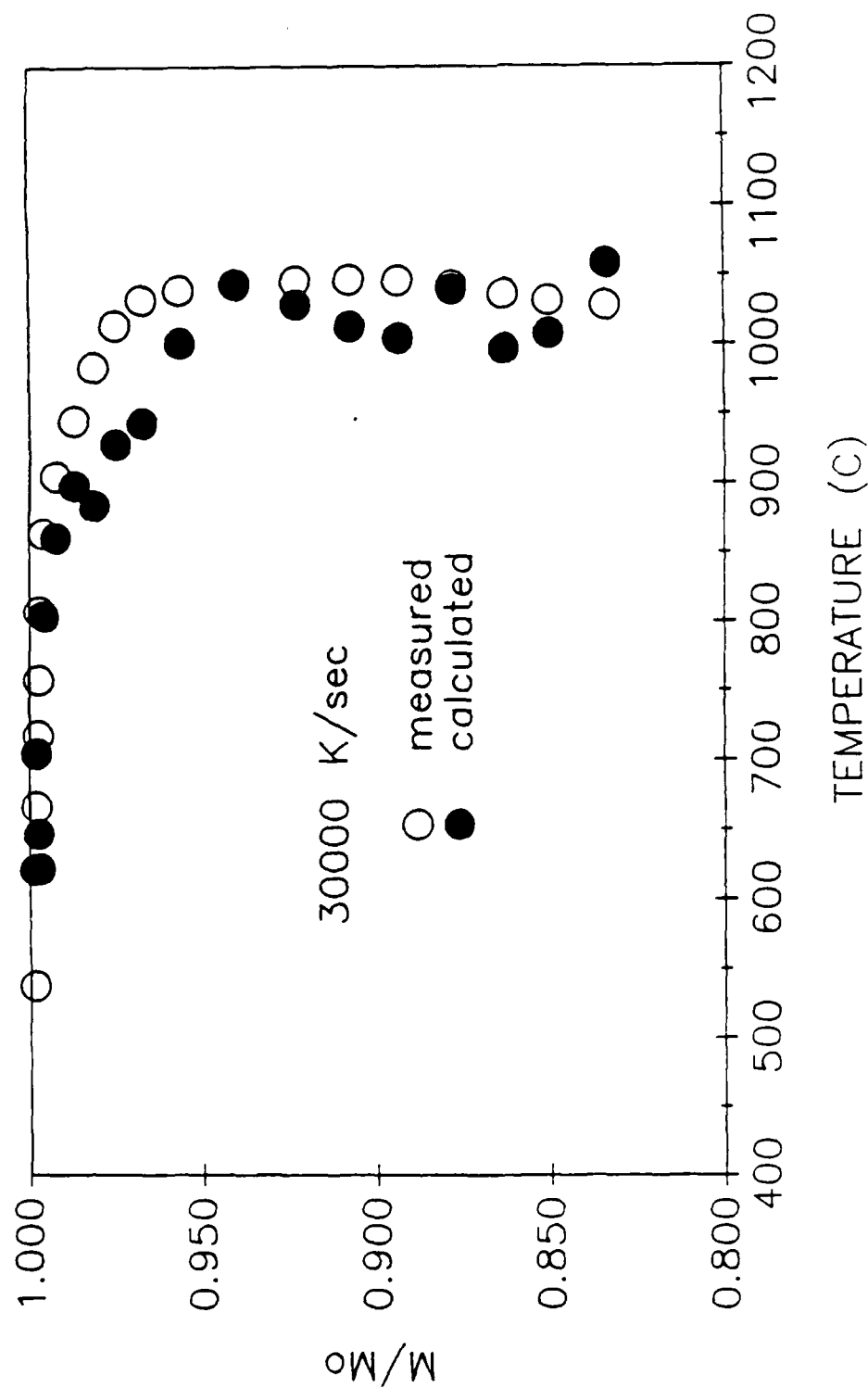
Fig. 8 — Measured and calculated plots of M/M_0 as a function of temperature for a heating rate of 30000 K/sec. The theoretical plot was obtained by determining the temperature at which a particular mass fraction would be found using the parameters in Table 1. The average percent error between the calculated and measured points is 7%.
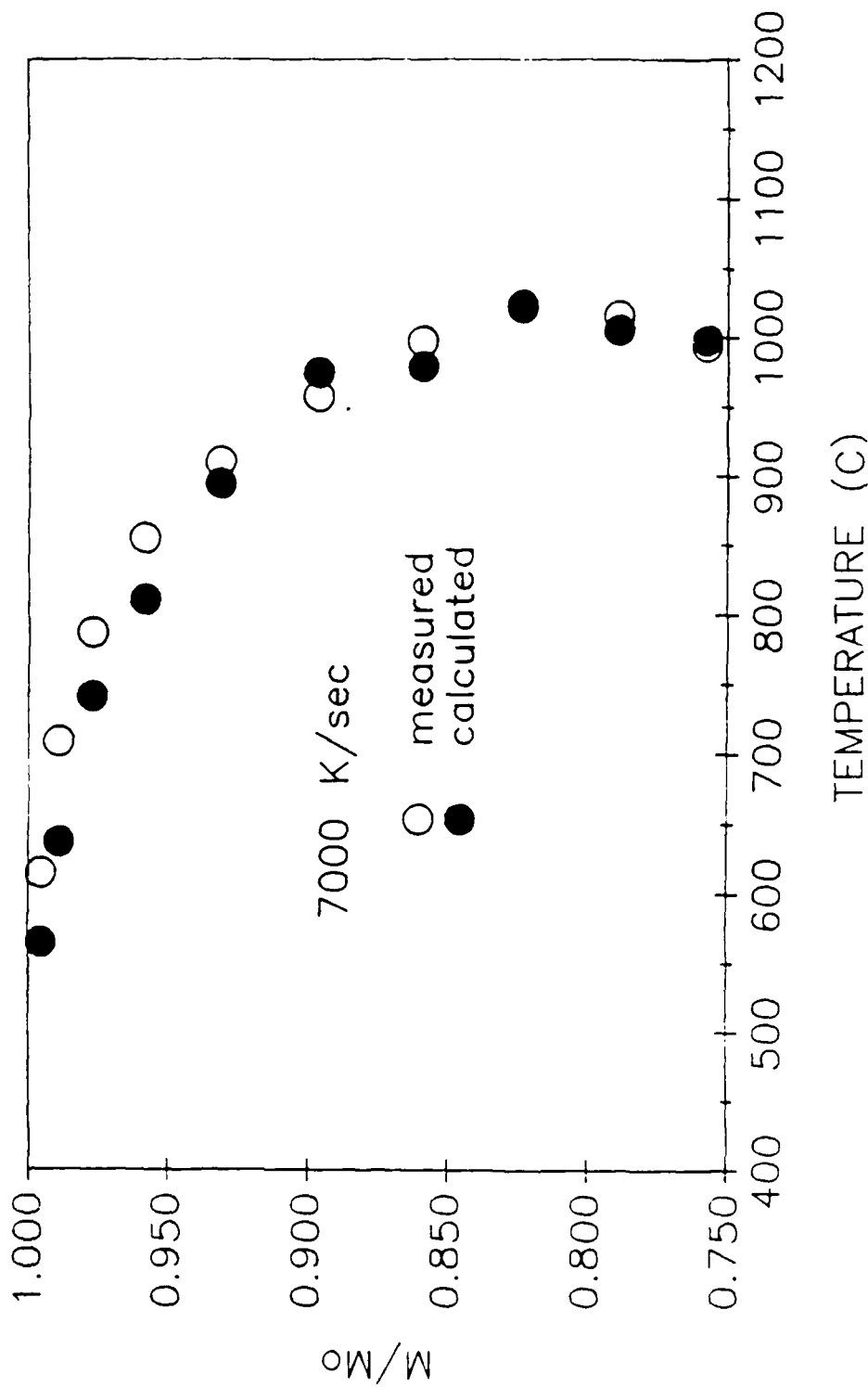
Fig. 9 Measured and calculated plots of M/M_0 as a function of temperature for a heating rate of 7000 K/sec. The theoretical plot was obtained by determining the temperature at which a particular mass fraction would be found using the parameters in Table 1. The average percent error between the calculated and measured points is 4%.
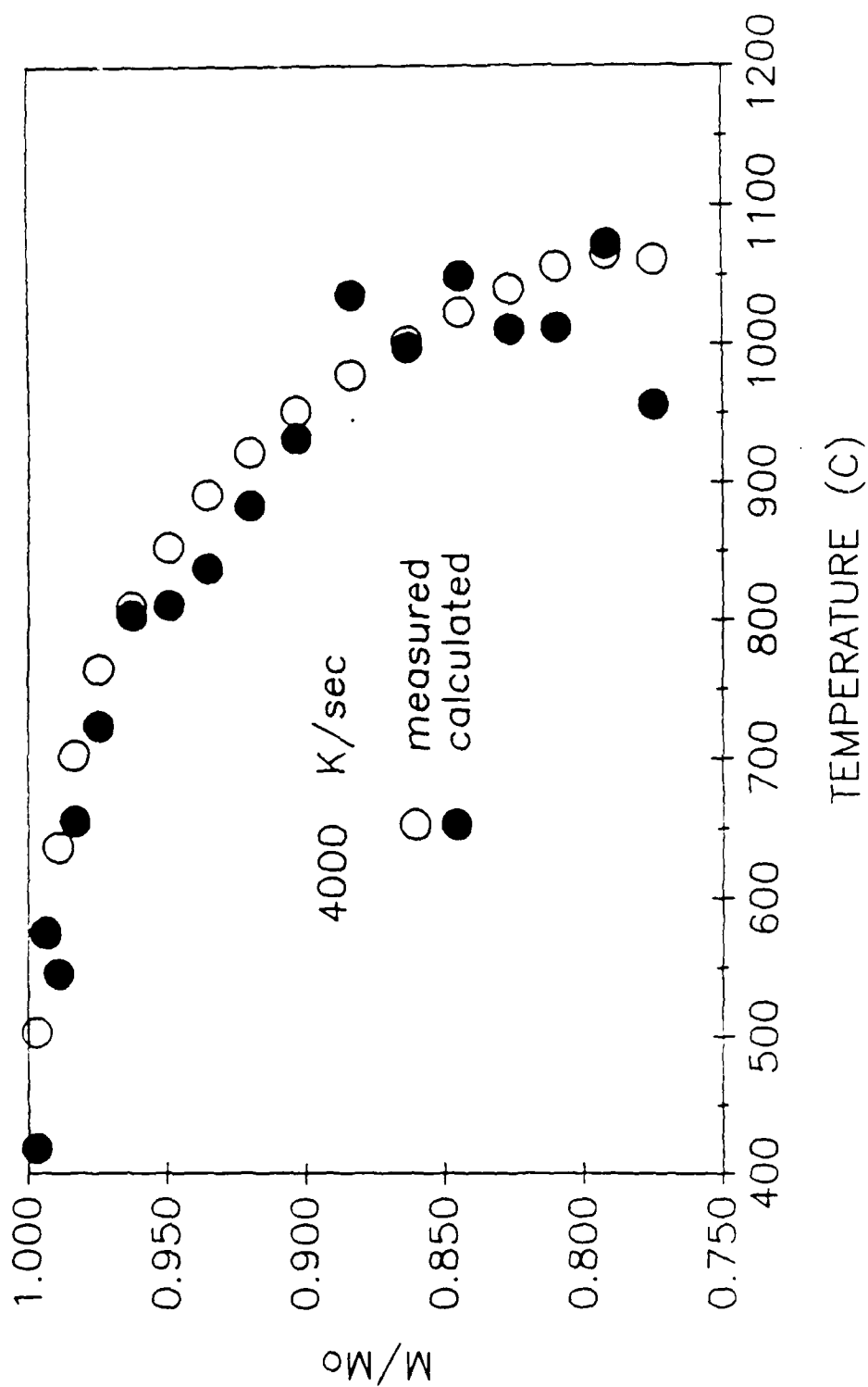
Fig. 10 — Measured and calculated plots of M/M_0 as a function of temperature for a heating rate of 4000 K/sec. The theoretical plot was obtained by determining the temperature at which a particular mass fraction would be found using the parameters in Table 1. The average percent error between the calculated and measured points is 5%.
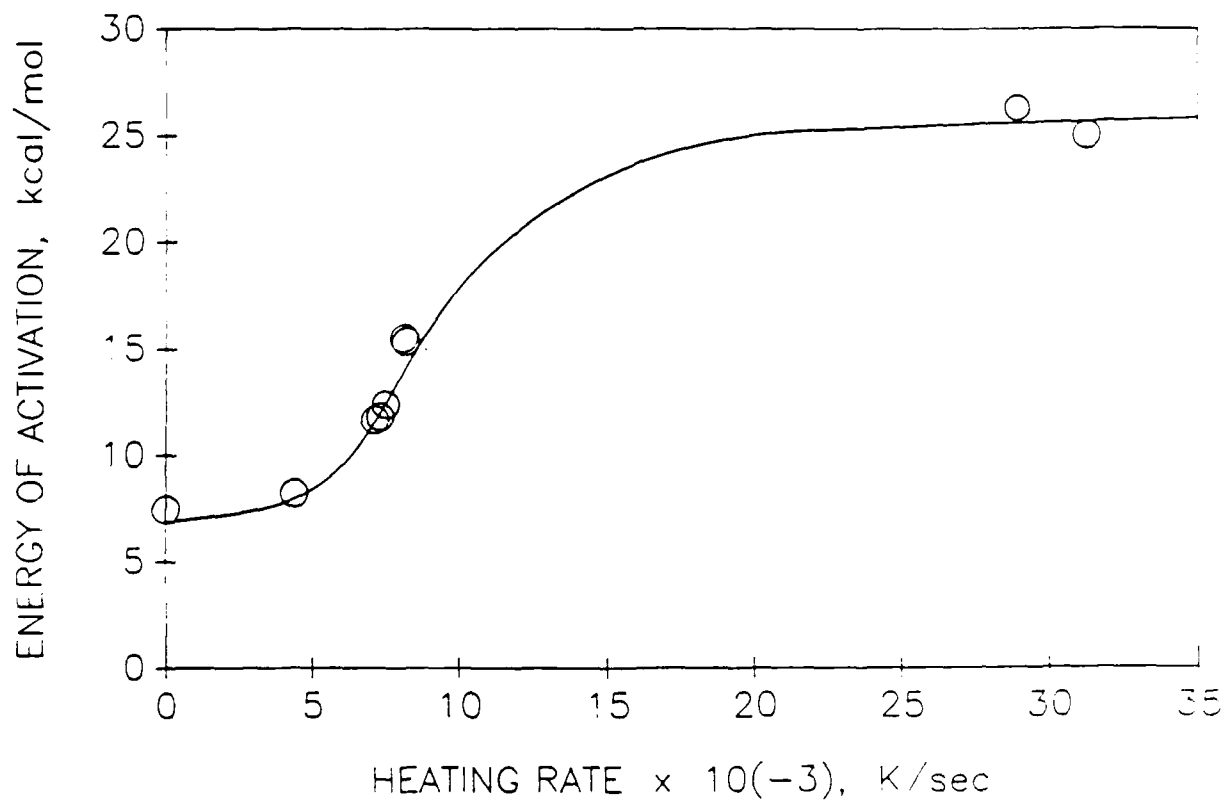
Fig. 11 — Energies of activation as a function of heating rate. The solid line curve is based on an assumed asymptotic behavior for the energy of activation at extreme heating rates — the low rate data is predominately one mechanism and the high rate data is another.